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Influence of processing conditions on the mechanical behavior of MWCNT reinforced thermoplastic nanocomposites

S. Doagou-Rad[a,b,*], A. Islam[a,b], J. S. Jensen[a]

[a]*Centre of Acoustic Mechanical Microsystems (CAMM), Technical University of Denmark, Building 352, DK-2800 Kgs. Lyngby, Denmark*
[b]*Department of Mechanical Engineering, Technical University of Denmark, Produktionstorvet, Building 427A, DK-2800 Kgs. Lyngby, Denmark*

* Corresponding author. Tel.: +45-4525-4867; fax: +45-4525-4700. E-mail address: sadora@mek.dtu.dk

Abstract

The influence of the processing conditions and MWCNT content on the mechanical properties of PA6,6-based nanocomposites are investigated. In addition to the composition of the composites, the impact of manufacturing conditions such as dilution mechanism, twin-screw extruder mixing specifications, and injection molding parameters on the behavior of the nanocomposites are evaluated. Results show that while the increase in the content of MWCNTs can lead to 40.0 % enhancement in the mechanical properties, changing the processing parameters varies the values by 30.0 % in the same content. The mechanisms involved in the modulation of the nanocomposites properties are also discussed.

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Keywords: Composites; Injection molding; Carbon nanotubes; Nanostructures; Thermoplastic; Polymer; manufacturing; Mechanical properties; Rheology

1. Introduction

Recent advancements in the realm of science and technology have created new possibilities and opportunities for different industrial applications. Among these novel possibilities, carbon nanotubes (CNTs) with their various extraordinary properties have attracted unprecedented interest of researchers and scientists from all over the world in the last two decades. Since their discovery in 1991, significant research has been underway to study their unique properties [1–3]. In fact, because of their exceptional properties such as mechanical, electrical, thermal, etc. features, composites reinforced with CNTs are being considered as the replacement to many conventional materials in various industrial applications including automotive, aerospace, sport equipment, energy, and infrastructure sectors [4]. However, despite their increasing applications, lack of extensive research that is mainly targeting tailored manufacturing of these materials especially in the industrial scales can be noted easily. In fact, there are just a few papers that have focused on the behavior of the CNT reinforced nanocomposites manufactured through industrially viable techniques [5–8]. It is also noteworthy to mention that the main focus of most of these few papers were the electrical properties of the polymeric nanocomposites.

Polyamide or Nylon 6,6 (PA 6,6) is one of the most well-known engineering polymers with different applications in various industrial sections especially automotive industry. Some prominent properties such as good mechanical behavior, fair heat and fatigue resistances, low-temperature behavior, resistance to oils, fair cost, stability in the manufacturing processes, etc. have made PA 6,6 and reinforced PA6,6 one of the most consumed polymers in the world. In recent years, regardless of their particular susceptibility to humidity, they are replacing metal components in various applications where they are offering better mechanical and chemical performances with less weight [9].

Injection moulding of components from thermoplastic polymers is a preferable and established industrial production method because of its considerable advantages in cost and time. However, the involved parameters in this process can notably influence the properties of polymeric composites. Nanocomposites reinforced with Multi Walled Carbon Nanotubes (MWCNTs) are considerably influenced by the

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defined state of the polymer and nanofillers during both melt and cooling states. In fact, the properties of the nanocomposites are highly influenced by the distribution, dispersion, alignment, and the interfacial properties of MWCNTs in the polymer system. In other words, parameters such as injection speed, injection pressure, melting temperature and mould temperature define the quality of the nanocomposites [6,9,10]. Moreover, it should be noted that based on the specific targeted properties, the state of MWCNTs in the nanocomposites should be tailored differently. However, despite their soaring applications in different industries, only a few papers have focused on the sensitivity of the final behaviors as a result of the different manufacturing processes.

The purpose of this study is to investigate of the influence of the manufacturing process parameters on the mechanical properties of polymeric nanocomposites. PA 6,6-based nanocomposite specimens with different contents of MWCNTs were prepared via different methods. Subsequently, the prepared specimens were characterized using uniaxial tensile experiments and the influence of the processing parameters i.e. dilution and injection molding parameters on the mechanical behavior were studied in detail. In order to find the influential mechanisms on the variations of the observed mechanical properties, rheological analyses and scanning electron microscopy (SEM) were employed.

2. Experiments

2.1. Materials

The multi-walled carbon nanotubes used in this study are catalytic chemical vapor deposition produced thin MWCNTs (NC 7000 ^{TM}) by Nanocyl SA, Belgium, with the average aspect ratio of 67 (d_{ave}*=10.4 nm*) [5]. The PA 6,6 based masterbatch containing 15.0 wt. % of the aforementioned MWCNTs (according to the supplier Nanocyl SA) were selected in the manufacturing processes to acquire the desired contents in the nanocomposites. The masterbatch was selected especially because of the application of industrial MWCNTs within the polymer, and viability for mass production. In addition, Altech PA 6,6 (ALBIS Plastic GmbH) was selected to mix with the masterbatch in the dilution process because of its high melt flow index which is assumed to facilitate the dispersion of the nano fillers in the matrix (Fig. 1. (a) and (b)).

2.2. Melt mixing

Melt compounding is a well-stablished and preferred method in the industrial scale production of nanocomposites because of its favorable features such as creating considerably less pollutant residuals, mass production, high speed, and less cost. This process consists of melting the selected polymer at high temperatures, and mixing it with the defined amount of nano additives through rotation and shear forces to reach the desirable content of the fillers in the matrix. However, the quality of the products depends on several parameters such as polymer characteristics, compatibility of the nanofillers and the matrix, interface behavior, etc. In order to study the influence of the dilution process on the mechanical properties of the nanocomposites two main approaches were compared. The first dilution method, which is called “direct method” in this paper from now on, is hand-mixing the master-batch and the neat polymer, which is followed by the subsequent melt mixing in the barrel of the injection unit of the injection molding machine. In fact, in this process, the two different pellets are melted, and mixed simultaneously under heat, rotation and shear force originating from the hot rotating screw just before injection into the mold. This method has especially been favorable in mixing different colorants with polymers. The second method is the application of twin-screw extruder before injection molding to mix the two different polymeric pellets, and preparing the new compounds.

The conical counter rotating twin-screw extruder (HAAKE^{TM} Rheomex CTW, Φ=31.8/20 mm rear/front, L=300 mm) was selected to perform the melt mixing process, since it is assumed that the high shear force would be beneficial for the de-agglomeration of the carbon nanotubes. Prior to feeding the materials into the extruder, the neat polymer and master batch pellets were weighted, and hand mixed to the desired contents, namely 0.5, 1.0, 3.0, 5.0, and 6.0 wt. % of MWCNTs. The mixtures were dried before and after the twin-screw extruder process for respectively 4 and 6 hours at 80 ºC in order to exclude any influence of humidity for either mixing or injection molding. The temperature distribution through the five zones (from feed section to die) kept from 265 to 280 ºC, with the average temperature of 275 ºC. The melting screw speeds were 15, 25, and 50 rpm, with residence times of 12, 8, and 4 min, respectively (Fig. 1. (c) and (d)).

2.3. Injection molding

Injection molding of the nanocomposite specimens was performed on Ferromatik, Milacron following the instructions of ISO 294-1 standard. The geometry of the cavity of the mold was dog-bone designed based on ISO 527-2 2012 standard. A series of experiments were conducted using a two level, four factor factorial design to investigate the influence of the four considered parameters on the mechanical properties of the nanocomposites. The four factors of injection velocity, melt temperature, mould temperature, and holding pressure were variated between the predefined minimum and maximum values through 16 experiments (see Table.1).

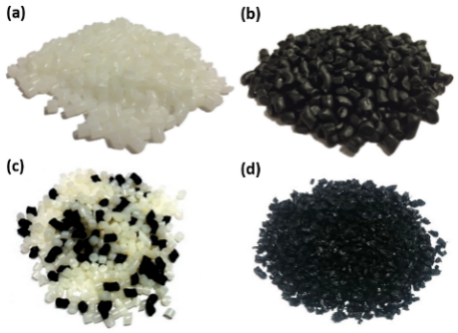

Fig. 1. (a) PA 6,6, (b) MWCNT filled masterbatch, (c) hand mixed masterbatch/ PA6,6, and (d) nanocomposite product of twin screw extruder.

The analyses of the results lead to the recognition of the importance of the first two parameters, namely injection velocity and melt temperature. Therefore, experiments followed by a new series of three-level, two factorial design on the first two parameters by the addition of the mid values in the considered range through 9 experiments.

Table 1 shows the used parameters in the injection molding experiments. At each experiment, after reaching to the stability, 35 samples were acquired, and stored in vacuum bags. A constant cooling time of 10 s was applied to all the experiments. The neat PA 6,6 was injection molded with the application of 100 mm/s injection velocity, 270 ^{o}C melt temperature, 60 ^{o}C mould temperature, and 60 bar holding pressure as the processing parameters.

Table 1. Set points of injection molding processes.

Levels	Factors			
	X_1 (mm/s)	X_2 (^{o}C)	X_3 (^{o}C)	X_4 (bar)
-	30	270	30	20
0	100	280	60	60
+	170	290	90	100

Characterization

In order to characterize the mechanical properties of the injection-molded specimens, uniaxial tensile experiments were conducted according to ISO 527-1 2012 standard. From each series of specimens produced via the defined setting and content, 10 samples were selected randomly, and were tested in the dry as molded state.

Furthermore, in order to study the dispersion state and other possible involved mechanisms in the behavior of the nanocomposites produced via different methods, scanning electron microscopy (SEM) (Quanta FEG 200 ESEM) was employed on the fractured surfaces of the nanocomposites using a charge-based method.

Melt rheological properties of the nanocomposites were acquired from the experiments conducted in AR2000 rheometer (TA Instruments). In order to prepare the 25 mm disc-shape samples, granulates of the nanocomposites were compression molded between the preheated plates for 6 min. Subsequently, the oscillatory shear measurements were performed in nitrogen atmosphere, using 25 mm parallel plates with 1.0 mm gap in between. Each experiment was conducted on three different samples using strains within the linear viscoelastic range, which had already been defined using strain amplitude sweeps.

3. Results and discussions

3.1. Effect of mixing method

The dispersion state in the polymeric nanocomposites is one of the defining parameters in the behavior of the nanostructured materials. In fact, the nanomaterials need to be distributed and dispersed effectively to be functional and deliver the expected benefits to their matrix system. Conducting this scenario in the polymeric nanocomposites filled with carbon nanotubes is a complex procedure, which depends on many different and interacting parameters including initial size of agglomerates, bonding strength of the nanofillers, type of polymer, interfacial characteristics, etc.

In fact, strong Van der Waals attractive forces along with the frictional forces arising from entanglement between the tubes makes reaching to an acceptable dispersion state a challenging endeavour. The specific geometry of carbon nanotubes -small diameters (order of several nanometers), and relatively long tubes (order of hundred nanometers or several micro meters) - with their high aspect ratios causes additional difficulties in comparison to other nanoparticle aggregations. It is known that weak Van der Waals forces are proportional to the inverse of the radius of the particles [12]. Therefore, the small size of the carbon nanotubes magnify these forces significantly. In fact, the Van der Waals attraction forces for particles with the average diameters of 10 $nm - 1.0$ μm are $10^8 - 10^4$ time stronger than the gravitational forces [13].

In order to break up the alien agglomerates, and reach to their effective size, the external stress acting on the agglomerates should exceed the strength of the aggregates. In other words, shear forces arising from the screws in either twin-screw extruder or injection molding machine, should overcome the agglomerate strength. Following the wetting and infiltration steps, if the shear stress in the melt is more than the agglomerate strength, dispersion process through either rupture or erosion mechanisms initiates.

In order to compare the different setting and methods of melt compounding, the nanocomposites containing 6.0 wt. % of the MWCNTs were selected. In fact, as the amount carbon nanotubes in the polymer matrix increases, acquiring a proper dispersion becomes harder due to several interacting parameters including the mentioned high surface energy of the CNTs, notable increase in the viscosity of the molten mix, and the decrease in the average distance of the individual carbon nanotubes. Studies in the area of the nanocomposites have introduced different limits for the enhancement capability of the carbon nanotubes [2,3]. In other words, usually after a certain content of carbon nanotubes, poor dispersion state and larger sizes of agglomerations inhibit further improvement in the properties. However, based on the applied manufacturing method, the polymer characteristics and the used CNT specifications, the bounds of enhancement vary noticeably. Fig. 2. shows the comparison between the mechanical behaviors of the nanocomposites containing 6.0 wt. % MWCNTs produced through the two mentioned dilution methods.

As it is evident from the diagrams, the elastic moduli of the nanocomposites produced from the two different methods are nearly similar, and notably higher (~ 40 %) than the elastic modulus of the neat PA 6,6. Despite the fact that the elastic moduli of the nanocomposite made from the two different methods are nearly similar (the difference is less than 4%), their tensile strengths are completely different. In fact, the tensile strength of the nanocomposites manufactured incorporating the direct method were not only less than the ones in the products of the other dilution method, but also they presented strengths even less than pure PA 6,6.

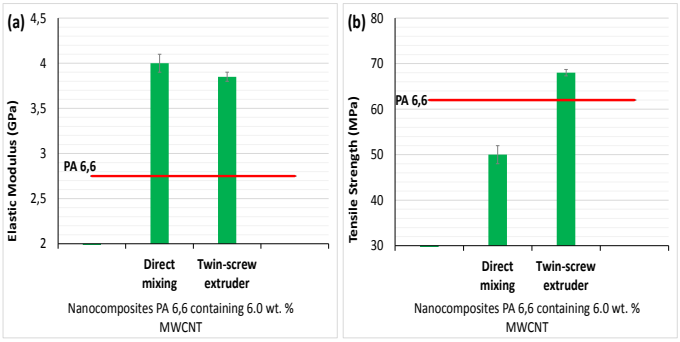

Fig. 2. Comparison between the direct mixing and the twin-screw extruder dilution methods: (a) elastic modulus, (b) tensile strength.

Fig. 3. (a) and (b) show the dispersion states of the fractured surfaces of the nanocomposites diluted via the direct and the twin-screw extruder methods. It can be clearly seen from the SEM images that the dispersion states in the two nanocomposites with same content of MWCNTs (6.0 wt. %) are completely different. In the nanocomposites processed via the twin-screw extruder, carbon nanotubes are fairly well distributed and dispersed. In contrast, in the nanocomposites diluted directly in the injection molding machine, separate islands of carbon nanotubes can be seen. Indeed, it seems that the shear forces arising from the injection molding screw was not solely enough to break agglomerations down efficiently in the system. Hence, agglomerations with the average diameters of 4 μm are distributed in the matrix, which are acting as micro stress concentrations resulting in the tensile strengths even less than the neat PA 6,6 (see Fig. 3. (c)).

In addition, in order to study the involved parameters in the twin screw extruder process i.e. rotation speed and melting temperature, further investigations were performed. Fig. 4 depicts the influence of melting temperature and rotation speed on the tensile strengths of the nanocomposite specimens, which have subsequently been produced via injection molding. Similar to the previous results, changing the aforementioned parameters was remarkably not influential on the elastic behavior of the nanocomposites. Furthermore, results showed that regardless of small change in the tensile strength of the specimens, increasing temperature is not changing the failure behavior of the nanocomposites significantly. It seems that just employing the shear stress in two consecutive steps (twin-screw extruder and injection molding) provides enough shear to acquire a fair and stable dispersion state (see Fig. 4. (a)).

However, the influence of rotation speed seem to be completely influential on the tensile strength of the produced nanocomposites. In this respect, interesting results presented in Fig. 4. (b) is so enlightening. The results showed that with increasing the rotation speed, the mechanical properties are increasing initially, however, after reaching to maximum resulting from employment of a certain rotation speed, the properties are declining. It can be deduced that the increasing of the rotation speed and shear stress is in favor of de-agglomeration of the nano-additives in the polymer system, but further increase of the shear forces in the system is resulting into degradation of the polymer or shortening the tubes.

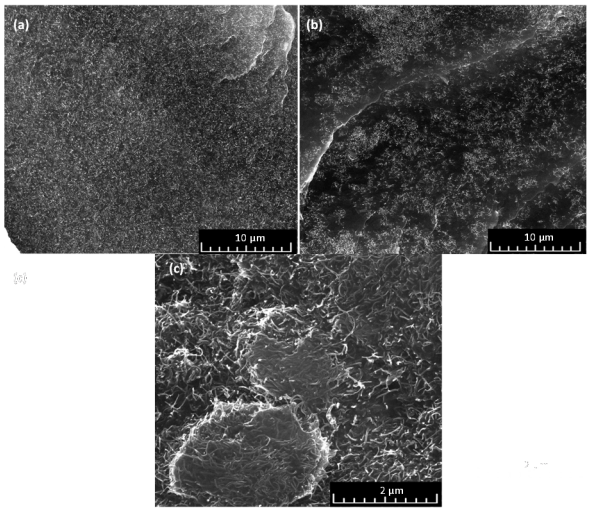

Fig. 3. Dispersion state in 6.0 wt. % MWCNT filled nanocomposites (a) processed in twin-screw extruder, (b) diluted via direct method, and (c) agglomerations in products of the direct method dilution.

It seems that high shear stress and strain in combination with lower degrees of extensional stress in high temperature atmosphere are inducing mechanochemical degradation to the molten composite system. The rate of this degradation and chain scissions depend on several parameters in addition to the shear rate and temperature, such as molecular weight, length of polymer chains, melt viscosity, and presence of oxygen or plasticizers [14].

3.2. Effect of injection molding parameters

Finding the appropriate method and setting for the dilution of the MWCNT filled masterbatches was followed by the investigation on the effect of injection molding parameters on the mechanical properties of the novel nanostructured materials. To perform this analysis, masterbatches were diluted to 3.0 wt. % of MWCNT in the PA 6,6 matrix, since it was believed that in this content the influence of agglomerations on the mechanical properties can be rather neglected. Therefore, no such an interference in the involved parameters and interpretation of the results is expected to be present. Fig. 5. shows the effect of melt temperature on the elastic modulus and tensile strength of the PA 6,6 based nanocomposites reinforced with MWCNTs. Results are demonstrating a noticeable decline in the mechanical properties with increasing the injection molding melting temperature.

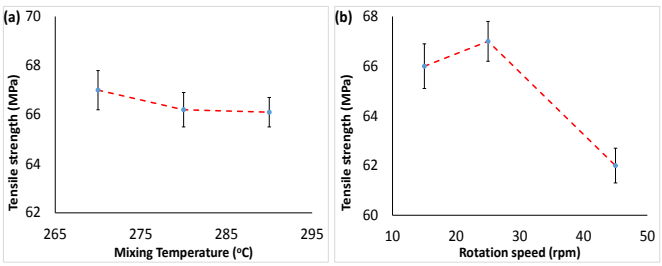

Fig. 4. (a) Effect of mixing temperature, and (b) rotation speed on the tensile strength of 6.0 wt. % MWCNT filled nanocomposites.

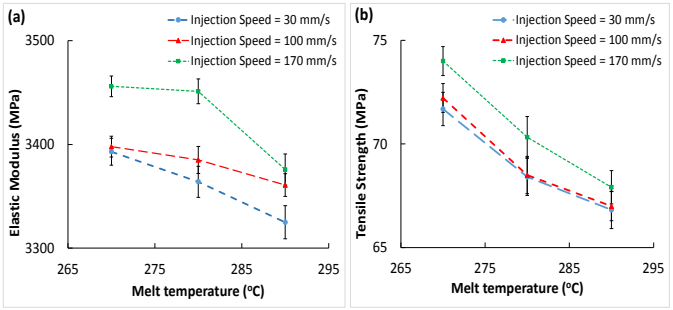

Fig. 5. Influence of melt temperature on the (a) Elastic modulus, and (b) tensile strength of 3.0 wt. % MWCNT filled nanocomposites.

Rheological studies on the nanocomposites containing 3.0 wt. % of carbon nanotubes might clarify the reason behind this behavior to some extent. As it is obvious from Fig. 6. data points, increasing the melt temperature is causing a reduction in viscosity, which was expected. However, the interesting part of these curves is the two extremes of the frequency scope. In the high frequencies, the complex viscosities in different temperatures are close to each other, which results in similar levels infiltration of polymer chains in the carbon nanotubes agglomerations. In other words, the maximum size of agglomerations regardless of the melt temperatures is expected to be similar. However, the difference in the viscosity increases in lower frequencies, which is corresponding to the final stage of injection molding and composite residing in the mold. Indeed, the melt behavior in this stage defines the final microstructure and alignment in the composite system. It can be deduced that the higher viscosities at the lower temperatures facilitate the alignment of the polymer chains and carbon nanotubes in their final settlement, resulting into the notable increase in the mechanical properties. It should be also mentioned that although PA 6,6 is a semi-crystalline polymer, the crystallinity parameter and its influence on the properties has not investigated in this paper.

Fig. 7. depicts the effect of injection speed on the mechanical properties of the nanocomposites. As it can be seen clearly from the diagrams, increasing the injection speed is improving the mechanical properties of the nanocomposites. However, the amount increase is less comparing to the observed enhancement as the function of melt temperature. Although increasing the injection speed promotes the alignment of the tubes and polymer chains,

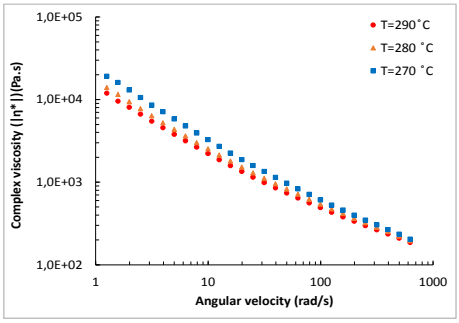

Fig. 6. Complex viscosity of the 3.0 wt. % MWCNT filled nanocomposites as a function of angular velocity and temperature.

it also invokes a counteracting parameter simultaneously. In fact, raising injection speed increases the friction heat in system, which in turn decreases the viscosity and tubes alignment. Nevertheless, it seems that the summation of these counteracting parameters is toward increase in the alignment and improvement of the mechanical behavior eventually.

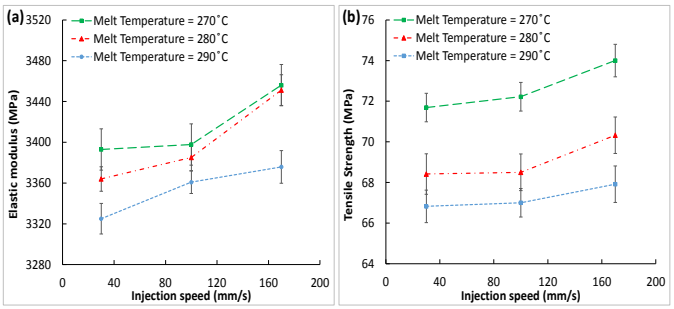

Fig. 7. Influence of injection speed on the (a) elastic modulus, and (b) tensile strength of 3.0 wt. % MWCNT nanocomposites.

The influences of the two other studied parameters on the mechanical properties of the nanocomposites are illustrated in Fig. 8. Although increasing holding pressure is resulting in the enhancement of tensile strength, the rate of improvement is also a function of melting temperature (see Fig. 8. (a)). In other words, the slope of the enhancement as the function of holding pressure is decreased in elevated temperatures. While, the influence of holding pressure on the tensile strength of the nanocomposite reinforced with 3.0 wt. % MWCNTs is negligible at $T_{melt} = 290^{o}C$, it becomes more noticeable at $T_{melt} = 270^{o}C$. Furthermore, as it is evident from Fig. 8. (b) results, the influence of mould temperature on the tensile strength of the polymeric nanocomposites is not discernible. One might explain this trend to very high crystallinity temperature of the PA 6,6 and the corresponding composites. It is also noteworthy to mention that none of the aforementioned parameters (i.e. holding pressure and mould temperature) did change the elastic moduli of the nanocomposite considerably.

3.3. Effect of MWCNT content

Thereafter the nanocomposites with different contents of MWCNTs, namely 0.5, 1.0, 3.0 and 5.0 wt. % were produced according to the results of the previous sections.

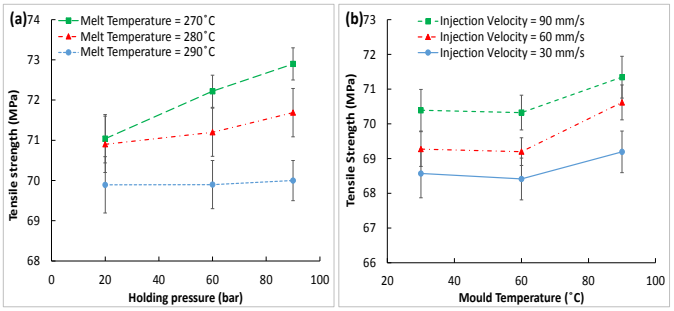

Fig. 8. Influence of (a) holding pressure, and (b) mould temperature on the tensile strength of 3.0 wt. % MWCNT filled nanocomposites.

Fig. 9. represents the influence of MWCNT content on the mechanical properties of the nanocomposites. Results showed that despite the slight reduction of the slope of enhancement, the elastic moduli of the nanocomposites increased persistently (~ 35 % by 5.0 wt. %) as the function of MWCNT content (Fig. 9. (a)). The same trend was also followed in the observed tensile strengths. However, the reduction in the rate of improvement were much more radical. In fact, after 18.0 % of enhancement in the tensile strength, the beneficial influence of carbon nanotubes on the tensile strengths were not present anymore (Fig. 9. (b)). It seems, regardless of the two consecutive mixing process, there are still some agglomerations in the system, which are acting as local micro stress concentration regions. Lack of further enhancement in the tensile strengths can be attributed to these detrimental regions in combination with lack of polymer chains/tubes alignment in higher contents of the nanotubes.

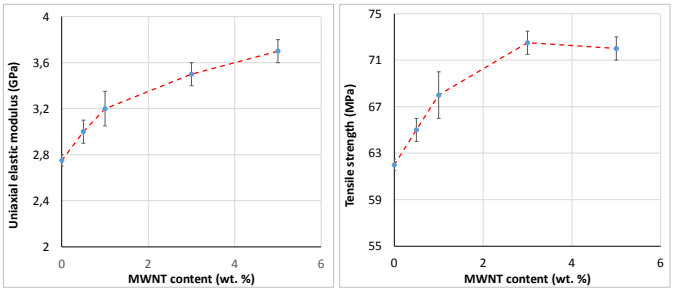

Fig. 9. (a) Elastic moduli, and (b) tensile strength of PA 6,6 based nanocomposites as the of the function of MWCNT content.

4. Conclusions

PA 6,6 based nanocomposites reinforced with different contents of multi walled carbon nanotubes were prepared through different methods. Investigations showed that the twin-screw extruder dilution method is remarkably more influential in the dispersion of nano-additives in the polymer matrix. However, further increase in the shear rate resulted in the polymer degradation and tube shortening. Moreover, influences of the four different injection molding parameters on the mechanical properties of the nanocomposites were studied in detail. Results showed that the low melt temperature, high holding pressure, and injection speed have positive influence on the mechanical properties of the nanocomposites. However, the enhancement rates and trends were different and dependent on different counteracting parameters. Excluding the melt temperature case, elastic moduli of the nanocomposites did not vary significantly. Eventually the influence of carbon nanotubes content on the mechanical properties was investigated. The results indicated 35 and 18 % increase in the elastic moduli and tensile strength with the addition of 5.0 wt. % MWCNT, respectively. However, the rate of enhancement decreased constantly with further addition of nanotubes. In addition to the relative growth of the agglomerations, this behavior was also attributed to the polymer chains and nanotubes reluctance to the imposed alignment.

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